PB-221 095

INVESTIGATION OF CORROSION-DEPOSITION PHENOMENA ON GAS TURBINE BLADES

WESTINGHOUSE RESEARCH LABORATORIES

PREPARED FOR
NATIONAL ENVIRONMENTAL RESEARCH CENTER

1973

Distributed By:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

BIBLIOGRAPHIC DATA SHEET	1. Report No. EPA-670/2-73-06	2.	PB 221 095

4. Title and Subtitle

INVESTIGATION OF CORROSION-DEPOSITION PHENOMENA ON GAS TURBINE BLADES

5. Report Date: 1973-issuing date

6.

7. Author(s): L. R. Fleisher

8. Performing Organization Rept. No.

9. Performing Organization Name and Address

Combustion Systems Research Group
Westinghouse Research Laboratories
Pittsburgh, Pennsylvania 15235

10. Project/Task/Work Unit No.

11. Contract/Grant No.: 68-03-0049

12. Sponsoring Organization Name and Address

U.S. Environmental Protection Agency
National Environmental Research Center
Office of Research & Development
Cincinnati, Ohio 45268

13. Type of Report & Period Covered: Final

14.

15. Supplementary Notes

16. Abstracts

The resistance of gas turbine components to the corrosive environment expected in a power plant fueled with shredded refuse has been questioned. Corrosion tests were run at conditions simulating those expected from the interfacing of a fluidized bed refuse combustor with current state-of-the-art gas turbines.

On the basis of these simulations, minimum projected lives on the order of 8,000 hours for the Ruston Series TA 1500 and 10,000 hours for the Westinghouse W-251 and G. E. MS 5000 turbines would be expected. No corrosion phenomena other than oxidation were observed despite the presence in the test environment of chlorine, sulfur, and alkali metal elements. These 100 and 300 hour test results are tentatively explained in terms of deposit spalling which prevents a build up of corrodents in an intact deposit.

17. Key Words and Document Analysis. 17a. Descriptors

Tests; Waste disposal; Wastes; Degradation; Recycling; Corrosion; *Corrosion tests; Refuse disposal; *Pilot model, *Corrosion resistance; Simulation; Combustion products; Gas turbines; Oxidation; Creep strength

17b. Identifiers/Open-Ended Terms

Solid waste disposal; Resource recovery; Ruston Series TA 1500; Westinghouse W-251 turbine; G. E. MS 5000 turbine; *Precipitate depletion; Fluid bed combustor; Deposit spalling; Creep resistance; *Metal degradation; CPU-400; Generating power

17c. COSATI Field/Group

Reproduced by
NATIONAL TECHNICAL INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

18. Availability Statement: Release to public

19. Security Class (This Report): UNCLASSIFIED

20. Security Class (This Page): UNCLASSIFIED

21. No. of Pages: ~~42~~ 39

22. Price: 3.75

FORM NTIS-35 (REV. 3-72)

USCOMM-DC 14952-P72

EPA-670/2-73-06
June, 1973

INVESTIGATION OF CORROSION-DEPOSITION PHENOMENA ON GAS TURBINE BLADES

By

L. R. Fleischer
Combustion Systems Research Group
Westinghouse Research Laboratories
Pittsburgh, Pennsylvania 15235

Contract No. 68-03-0049
Program Element No. 1D2063

Project Officer

Richard Chapman
Solid Waste Research Laboratory
National Environmental Research Center
Cincinnati, Ohio 45268

Prepared for
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

Preceding page blank

REVIEW NOTICE

The Solid Waste Research Laboratory of the National Environmental Research Center, Cincinnati, U.S. Environmental Protection Agency, has reviewed this report and approved its publication. Approval does not signify that the contents necessarily reflect the views and policies of this laboratory or of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

The text of this report is reproduced by the National Environmental Research Center, Cincinnati, in the form received from the Grantee; new preliminary pages have been supplied.

FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies of the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

As part of these efforts, this study investigated the resistance of gas turbine components to the corrosive environment of a power plant fueled with shredded refuse. On the basis of simulated conditions, the researchers were able to approximate minimum projected lives for the turbine parts involved and determine the amount of metal deterioration.

Andrew W. Breidenbach, Ph.D.
Director, National Environmental
Research Center, Cincinnati

TABLE OF CONTENTS

		Page
	ABSTRACT	1
1.0	INTRODUCTION	2
2.0	CONCLUSIONS	4
3.0	EXPERIMENTAL	5
	3.1 Thermal-Hydraulic Conditions	5
	3.2 Materials	6
	3.3 Corrosive Environment	9
	3.4 Test Equipment	12
4.0	RESULTS	14
	4.1 Weight Gain -- Deposit	14
	4.2 Weight Loss -- Scale	16
	4.3 Microstructure	17
5.0	DISCUSSION AND CONCLUSIONS	26
6.0	ACKNOWLEDGMENTS	30
7.0	REFERENCES	31
	APPENDIX A	32

Preceding page blank

LIST OF TABLES

I. Corrosion Test Conditions 5

II. Compositions of Gas Turbine Alloys 8

III. Flue Gas Analyses 11

IV. Flyash Analyses 11

V. Analysis of Deposit 16

VI. Corrosion At 1600°F, 105 PSIA, 100 Hours Exposure..... 25

LIST OF ILLUSTRATIONS

1. High pressure corrosion test passage (turbine simulator)..... 13

2. Air foil shape specimens at four stages of testing..... 15

3. Microstructures of Nimonic 80A..... 18

4. Microstructures of Nimonic 105..... 20

5. Rates of metal degradation in turbine simulator corrosion test.. 21

6. Microstructures of cobalt base alloys after 100 hours in the turbine simulator at 1600°F, 105 psia..... 23

7. Microstructures of nickel base alloys after 100 hours in the turbine simulator at 1600°F, 105 psia..... 24

INVESTIGATION OF CORROSION-DEPOSITION PHENOMENA ON GAS TURBINE BLADES

L. R. Fleischer
Combustion Systems Research Group

ABSTRACT

The resistance of gas turbine components to the corrosive environment expected in a power plant fueled with shredded refuse has been questioned. Corrosion tests were run at conditions simulating those expected from the interfacing of a fluidized bed refuse combustor with current state-of-the-art gas turbines.

On the basis of these simulations, minimum projected lives on the order of 8,000 hours for the Ruston Series TA 1500 and 10,000 hours for the Westinghouse W-251 and G. E. MS 5000 turbines would be expected. No corrosion phenomena other than oxidation were observed despite the presence in the test environment of chlorine, sulfur, and alkali metal elements. These 100 and 300 hour test results are tentatively explained in terms of deposit spalling which prevents a build up of corrodents in an intact deposit.

1.0 INTRODUCTION

The utilization of the stored chemical energy in refuse for power generation has received considerable attention in recent years. Most of the plants conceived or built in Europe or North America have been based on steam boilers wholly or partially fueled with refuse. These enterprises have demonstrated improvements in the environmental and economic aspects of waste disposal.

A refuse burning, power generation system under development by Combustion Power Company (CPC) of Menlo Park, California, is conceived to expand high pressure combustion gases directly through a gas turbine. The interaction of the combustion products with the inlet stage materials of three specific industrial turbines is the subject of this report.

Under the sponsorship of the U. S. Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio (EPA, NERC Cincinnati), CPC has conducted a system study and is currently developing a one-tenth scale pilot plant to demonstrate the feasibility of the system. Specifically CPC is designing and constructing the solid waste subsystem, fluid bed combustor, particle separators and automatic control system to interface with a conventional gas turbine, replacing the usual turbine combustors.

For the pilot plant a Series 1500 TA machine of the Ruston Turbine Division of English Electric Diesels, Ltd., Lincoln, England will be used. Larger machines considered potentially suitable for the prototype application are the MS 5000 model of the General Electric Gas Turbine Division, Schenectady, N.Y., and the W-251 of the Westinghouse Electric Small Steam and Gas Turbine

Division, Lester, Pa. The specifications for these machines determined the materials tested and the thermal-hydraulic environmental parameters of the tests. The chemistry of the environment was specified by CPC based on their fluidized bed combustion experiments.

2.0 CONCLUSIONS

Conservative extrapolations of the data indicate that useful machine operating lives of about 8,000 hours for the TA 1500 and about 10,000 hours for the MS 5000 and W-251 can be expected. These estimates are based on an allowable metal wastage of 20 mils and 40 mils respectively during the period of service and assume that the actual operating environment was well represented by the turbine simulator testing. By comparison, these machines operated with high-quality fuels under near-ideal conditions, would be expected to operate about twice as long before reblading became necessary.

The criterion used for determining metal deterioration in alloys used for stationary components was the depth of internal oxide penetration. The corresponding criterion used for alloys used for rotating parts was the loss of precipitated strengthening phases.

No attack other than oxidation was observed, i.e., no sulfidation or "hot-corrosion". Oxide scales were left intact even though the deposit spalled and no localized attack was found other than the normal penetration of oxide at grain boundaries.

3.0 EXPERIMENTAL

3.1 Thermal-Hydraulic Conditions

The temperatures, pressures, flow velocities, and sample materials for each test are listed in Table I. The turbine inlet conditions for the Ruston machine[2] are based on a 100,000 hour design life limited by creep failure. The other test conditions are close to published turbine inlet parameters but limited by the capacity of the test equipment.

TABLE I -- CORROSION TEST CONDITIONS

	Ruston	G.E.	Westinghouse
Temperature, °F	1450	1600	1600
Pressure, psia	57	105	105
Flow rate, ft/sec	528	500	500
Rotor Alloy	Nimonic 105	Udimet 500	Udimet 710
Stator Alloy	Nimonic 80A	FSX-414*	X-45

* FSX-414 is a G.E. patented alloy.

The corrosion samples were tested in two batches, one at the Ruston conditions and the other at the conditions jointly appropriate for the G.E. and Westinghouse turbines. During the corrosion tests, the pressures and flow rates were maintained close to the values in Table I. All samples in each batch were exposed to the same, uniform pressure and flow conditions.

The corrosive atmosphere was generated by burning impurity doped diesel fuel (see Section 3.3) in a gas turbine combustor. This arrangement did not provide a uniform gas temperature. Ideally, the temperature in this type of combustor is a maximum in the center and a minimum at the periphery, adjacent to the combuster wall. In practice, this was generally the case, but the temperature distribution was not symmetrical. Measurements in the mixing region upstream of the sample location indicated a temperature spread on the order of 400 °F. The temperatures were controlled by the extent of pre-heating the inlet air such that the volume weighted mean temperature matched the conditions of Table I. In addition, the positions of the individual samples were changed at 20 to 25 hour intervals. This rotation gave each sample in a batch an equivalent cumulative exposure history.

Throughout the tests, the concentration of impurities in the fuel and the air to fuel ratio were held constant. In this way, the impurity concentrations in the combustion gas were constant independent of pressure, flow, and temperature. However, the chemical form of the impurities and their partitioning between gas and solid phases may have varied with these parameters.

3.2 Materials

The alloys used in the Ruston series 1500 TA turbines, Nimonic 80A and Nimonic 105 were provided through the good offices of the International Nickel Company. The materials received were machined, cleaned, and tested without heat treatment. The tests, then, were made on machined surfaces of as-wrought metals.

The FSX-414 alloy was provided to the EPA by the General Electric Company. This material was machined, but otherwise tested as-received.

The other alloy samples were machined from stock cast or wrought and heat treated by the Howmet Corporation. The heat treatments

were designed to recover the effects of working and to optimize the volume fractions and particle sizes of the precipitated phases.

The specified compositions of the alloys tested are given in Table II.

These alloys were selected as representative of a wider selection of materials considered as current state-of-the-art for the turbines under consideration. Seven alloys were suggested by General Electric[3]; a similar number are in use at Westinghouse. The number of alloys to be tested was limited by the scope of the project so selection was based on typicality and wide usage, i.e., being in use by both Westinghouse and G.E. Note, however, that all of these alloys were developed for use in turbines using conventional fuels: distillate oil or natural gas.

TABLE II. COMPOSITIONS OF GAS TURBINE ALLOYS

Alloy Constituents, Weight Percent

	Ni	Co	Cr	Fe	Al	Ti	Mo	Mn	C	Si	B	W	Others
Nimonic 80 A	Bal.	2.0	18-21	5.0	0.5-1.8	1.8-2.7	-	1.0	0.1	1.0	0.008	-	Zr added
Nimonic 105	Bal.	15.0	13.5-16.0	2.0	4.2-4.8	0.9-1.5	4.5-4.8	1.0	0.2	0.5	added	-	Zr added
X-45	10.5	Bal.	25.0	2.0	-	-	-	1.0	0.25	-	0.10	7.0	
FSX-414	10.0	Bal.	29.0	1.0	-	-	-	-	0.25	-	0.005	-	
Udimet 500	Bal.	19.0	19.0	4.0	3.00	3.0	4.0	0.20	0.08	0.3	0.030	-	
Udimet 710	Bal.	15.0	18.0	-	2.5	5.0	3.0	-	0.07	-	0.020	1.5	

3.3 Corrosive Environment

The system simulated -- the CPU-400 plant -- includes several features to mitigate the variability and corrosiveness of the combustion gases fed to the turbine. Before combustion, the refuse is to be shredded, dried, and air classified. These steps will produce a well-mixed fuel with a fairly homogeneous size distribution, with a consistent moisture content, and with metals, glass, and rocks removed[1]. Use of a fluidized bed combustor is expected to provide essentially complete combustion of the shredded, dried refuse.

Between the fluidized bed combustor and the turbine, multiple stages of inertial separators or a combination of inertial, electrostatic, and mechanical separators will remove a substantial portion of the potentially corrosive flyash from the flue gas.

To quantify these expectations, a laboratory scale system was operated by CPC and the flue gas analyzed[4]. Appropriately pretreated refuse was burned in a fluidized silica sand bed at relatively low pressure. The combustion gases were passed through an inertial separator before analysis. The major flue gas and flyash constituents found by CPC are given in Tables III and IV. They recommended[4] that simulation of fluidized bed combustion products for turbine materials testing be limited to these constituents. The CPC report also recommended that a flyash concentration of 1.9 ppm (by weight) was appropriate to the fluidized bed system including particle separators.

It was deemed impractical to attempt an exact simulation of the fluidized bed combustion gases with an oil burning can combustor operated at several atmospheres pressure. Therefore, oil soluble contaminants were added to the fuel in amounts appropriate to reproduce the bulk analysis reported by CPC without attempting to control the partitioning of the individual elements. The additives used and

their proportions added are tabulated in Appendix A. The differences between the actual fluidized bed combustion gases and the turbine simulator combustion gas occurred for the following reasons:

- Combustion temperatures in the fluidized bed were about 1400°F with further combustion above the bed; maximum gas temperatures were about 1600°F. The turbine combustor used in the simulation operates with a flame temperature on the order of 3500°F with subsequent cooling by dilution with secondary air.
- The CPC test was conducted at pressures between one and two atmospheres. The turbine simulator corrosion tests were run at four and seven atmospheres.
- The fluidized bed combustor was operated with about six percent more air than was needed for complete combustion*. The turbine combustor was operated with 74 percent excess air.

The analyses of flue gas and flyash collected during the corrosion tests are compared to the CPC analytical data in Tables III and IV. The data tabulated represent an average of several samplings. It is clear that the flyash samples were contaminated with ferrous metals. This is likely to be a consequence of corrosion of the stainless steel sampling line. This observation is consistent with the low temperature, or "dew-point" corrosion found at the economizer or air heater exits of steam plants[5]. Attempts to determine the concentration of flyash in the gas stream were unsuccessful. The amounts of impurities added to the fuel were calculated to produce 1.9 ppm (by weight) flyash in the gas stream.

---

*Determined by oxygen balance on the flue gas analysis reported by CPC, Reference (4).

TABLE IV -- FLYASH ANALYSES

Ash Constituents as Oxides (Weight Percent)*

	$SO_4^=$	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	Fe_2O_3	Cr_2O_3	NiO	MnO
Ⓦ 1450°	.02	42.1	23.8	.6	2.8	2.7	7.9	19.1	trace	trace	trace
Ⓦ 1600°	4	14.1	10	2.7	6.4	4.6	.3	28.3	24.1	1.9	3.6
CPC	.24	43.9	27.8	5.6	3.3	11.2	3.3	5.6	-	-	-

* Flyash analysis by spark source mass spectroscopy

TABLE III -- FLUE GAS ANALYSES

Gas Stream Constituents (Volume Percent)†

	H_2	N_2	O_2	HC	Ar	HCl	CO_2	SO_2	CO	H_2O	NO_x
Ⓦ 1450°F test	.01	76.2	13.6	.01	.9	.01	4.5	N.D.	0.3*	4.8**	0.5*
Ⓦ 1600°F test	trace	77	16.0	.02	.97	.009	3.1	N.D.	0.2*	2.8**	0.6*
CPC	-	75	14.8	2.4	-	.009	5.2	.001	0.2	2.3	-

N.D. indicates Not Detected

* Taken from the results of on-line gas monitoring

** Derived from spectroscopic data by oxygen balance

† Flue gas analysis by mass spectroscopy

The fuel additives used to put intentional impurities in the system typically contain small amounts of other impurities. Low concentrations of the elements B, F, P, Cu, Pb, V, and Zn found in the flyash were attributable to this source. These minor constituents are generally considered corrosive; in particular, more than a few ppm V in fuel oil is considered highly deleterious[6]. Also, barium was detected in the tens to hundreds of ppm range. Barium is considered a corrosion inhibitor because of the stability of its sulphate. However, relative concentrations of Ba and $SO_4^=$ found in the flyash were such that less than one percent of the $SO_4^=$ could have been combined with Ba.

3.4 Test Equipment

The turbine simulator can be visualized as a long six-inch pipe. Air from a 300 hp rotary compressor is ducted through an indirectly fired pre-heater to the inlet end of the pipe. Diesel fuel is injected through a nozzle mounted in the upstream end of a six-inch diameter turbine combustor near the inlet. Downstream of the combustor is an array of thermocouples for measuring the temperature distribution in the gas stream, and a sampling tube for gas analysis. Further downstream, a transition section reduces the flow area to a 2 x 2-3/4 inch rectangular section. The corrosion specimens are exposed to the high velocity gas stream at this location. A back-pressure valve before exhaust allows control of the test pressure. These features are schematically illustrated in Fig. 1.

The samples tested were of two geometries. Pins of 1/4-inch diameter were used for corrosion measurement and microstructural analysis. Air foil shaped specimens were used as collectors of deposit simulating turbine blade flow patterns. These will be illustrated in the next section.

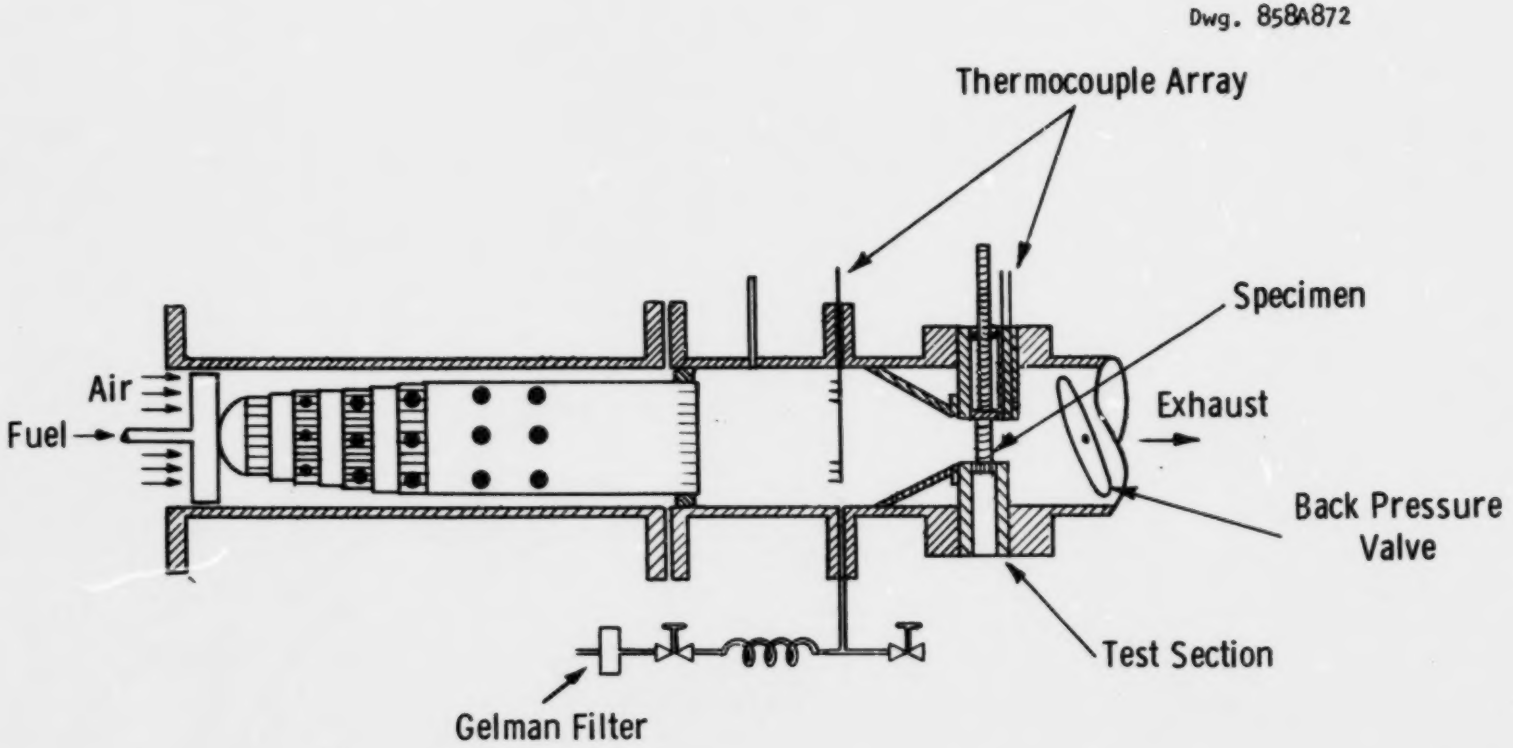


FIGURE 1 -- High pressure corrosion test passage (turbine simulator).

4.0 RESULTS

The four stages of sample life are illustrated in Fig. 2. The air-foil on the right is clean, untested metal. Next to it is a foil as it came from the turbine simulator coated with a layer of deposit. The third foil has had the deposit scraped off to expose the oxide scale at the surface of the metal. The far left specimen has had its scale removed by anodic dissolution exposing a pattern of metal oxidation. It can be seen that the heaviest attack occurred roughly in the center of the specimen area, indicating a temperature distribution similar to that desired in turbines: the high temperatures not coinciding with the highly stressed zones near the blade tip and the blade root.

4.1 Weight Gain -- Deposit

The specimens collected a light-tan, granular deposit. Initial rates of deposit accumulation were high, about 30 percent of the stabilized amount was picked up in the first 25 hours. The pick-up in the subsequent 25 hour periods were approximately 25, 15, 10 and 10 percent respectively. After 125 to 150 hours of exposure, the amount of deposit on each specimen stabilized in the range 30 to 45 mg/in^2 (5 to 7 mg/cm^2). The breadth of this range and the wide fluctuations in weight change from one test increment to the next indicate that after some build-up, the deposit spalls, or flakes off. Thus, the continuous build-up rate and the discontinuous loss rate give a discontinuous net weight change.

The spalling mode of deposit loss could directly expose the metal oxide surface to the combustion gases. However, visual examination of the specimens did not indicate any obvious areas of localized corrosion.

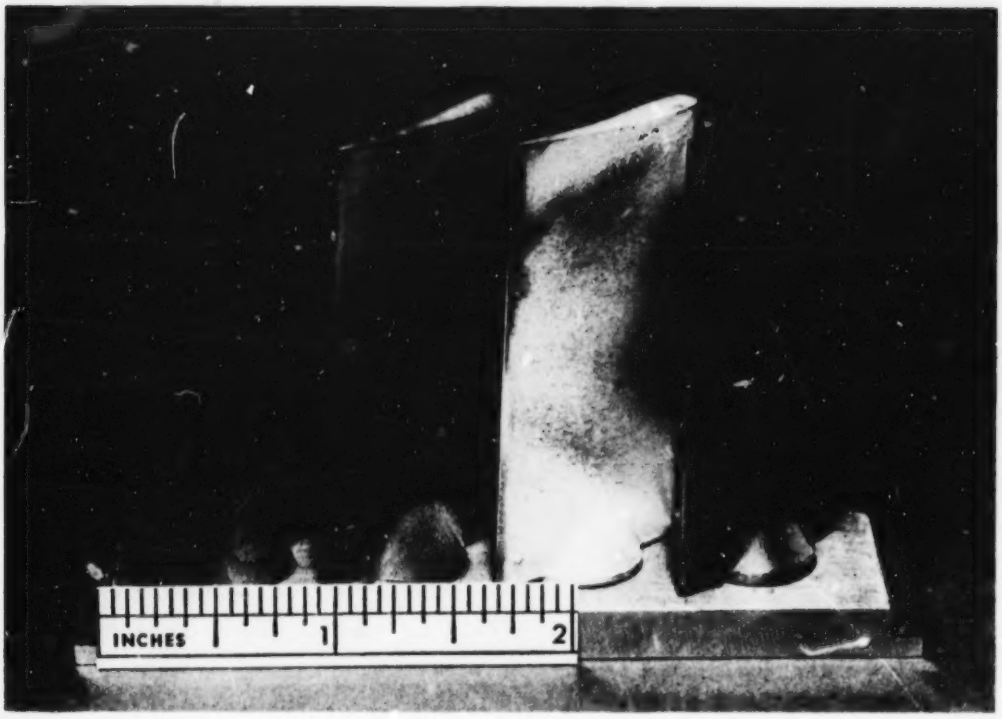


Figure 2 -- Air-foil shape specimens at four stages of testing: pre-test; as-tested; post-test with deposit removed; and post-test descaled (reading from right to left).

Three methods of analysis were used to characterize the deposits: x-ray diffraction, spark source mass spectroscopy, and x-ray spectroscopy with use of characteristic x-rays stimulated by electron bombardment in a scanning electron microscope (SEM).

Samples of deposit scraped from the 1450°F corrosion tests were submitted for x-ray diffraction analysis only. About 20 percent of the deposit sample proved to be crystalline. Two sets of diffraction lines were recognized. One of the compounds identified was tridymite,

a high temperature form of silica. The other set of lines was insufficient to make a definitive identification of the compound. It is, however, in the class of complex alkaline silicates typified by $CaAl_2(SiO)_2$.

The deposit from the 1600°F tests was better characterized. The major constituents identified by spark source mass spectroscopy are listed (as simple oxides) in Table V. The x-ray diffraction results again suggested, however, that more complex compounds were actually present. Ca_2SiO_4 was positively identified, and lines suggestive of alkaline sulfates were also observed. The sulfur detected by

TABLE V -- ANALYSIS OF DEPOSIT

Major Constituents as Simple Oxides (Weight Percent)

	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	Fe_2O_3	TiO_2	$SO_4^=$
Ⓦ 1600°F	49.7	24.4	2.8	5	1.4	2.6	0.4	1.3	12.4

mass spectroscopy is reported as sulfate ion. In addition to these major constituents, small amounts of other elements were measured including 100 to 200 ppm chlorine.

The SEM technique allowed analyses of the deposit *in situ*. It was found that the material varied from sample to sample and from place to place on any sample. Usually, silicon was the predominant element indicated, although in some places aluminum predominated. In one spectrum, silicon was the only significant contributor. Generally, however, signals from Si, Al, Ca, and Fe were recognized.

4.2 Weight Loss -- Scale

Weight loss measurements on descaled Nimonic alloy samples indicate losses to direct oxidation of the bulk alloy on the order of

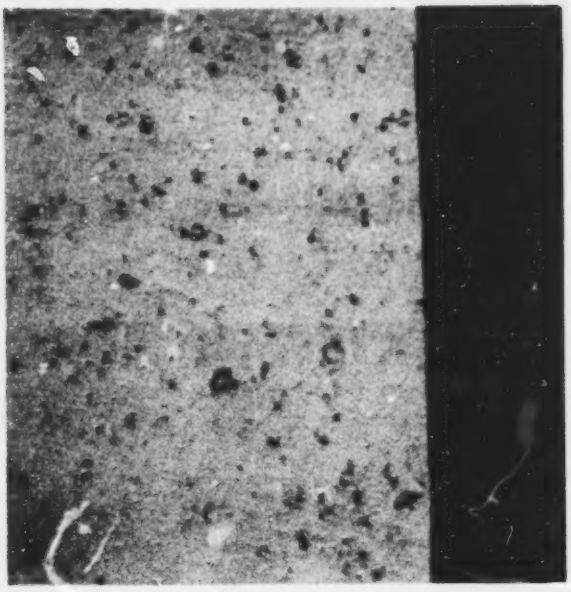
10^{-2} mg/cm^2-hr. This translates into a uniform surface recession on the order of 10^{-3} mils/hr. However, these estimates do not include the effective loss of structural metal due to metallurgical reactions beneath the remaining surface. These measurements proved to be highly dependent on descaling technique. There were not enough samples to impute a statistical significance to any weight loss found so the data were de-emphasized and the method not extended to the higher temperature samples. The extent of scaling was estimated by metallographic measurements.

4.3 Microstructure

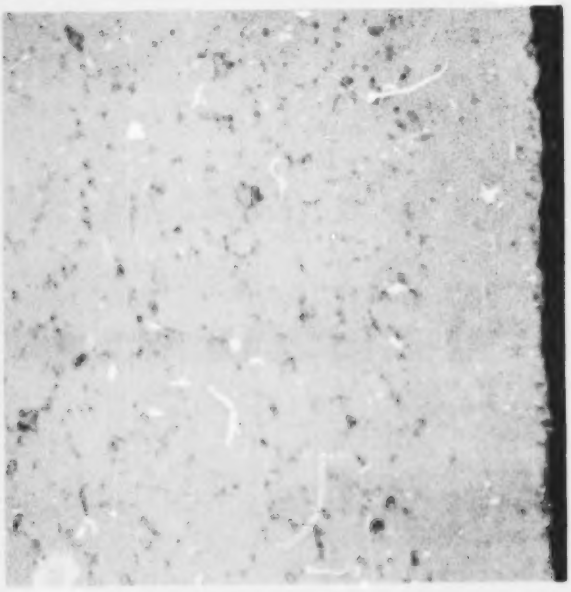
The diameters of sample pin cross-sections were determined with an optical comparator. This instrument is precise to about 0.0005 inches in the measurement of the close to 0.250 inch diameters. Comparison of the post-test measurements with pre-test diameters indicated no change within the precision of the instrument. It was concluded, therefore, that the oxidation of the samples caused less than half a mil change in the position of the surface. Thus, it was justifiable to base corrosion rate determinations on depths of metallographic features measured from the surface.

The microstructures of the cross-sections can be described in terms of two zones, or bands, which enclose the uneffected alloy. Closest to the surface is a band of alloy characterized by internal oxidation. In general, this is seen as penetration of oxide along paths of preferred mass transport and as the precipitation of oxides of alloy constituents with a high affinity for oxygen. The second band, continuous with the first, does not seem to be corroded, but is marked by an absence of the precipitated phases that are developed in the alloys to add strength to the metal.

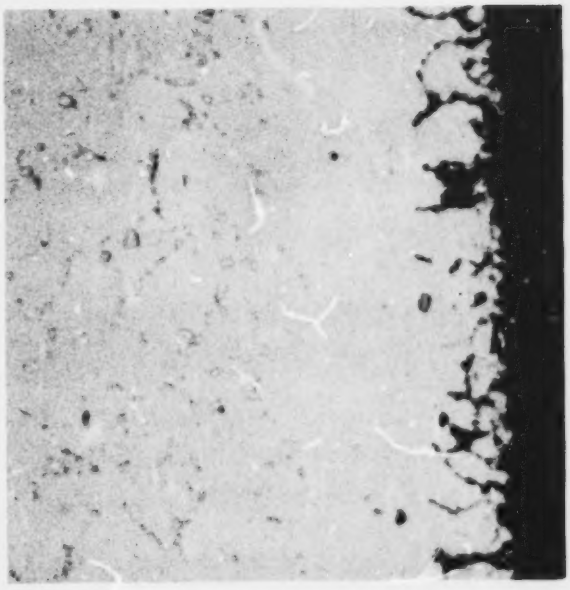
Microstructures of Nimonic 80A in four different conditions are shown in Fig. 3. All cases represent equivalent times and temperatures. Figure 3a is the structure of the alloy before heat treatment



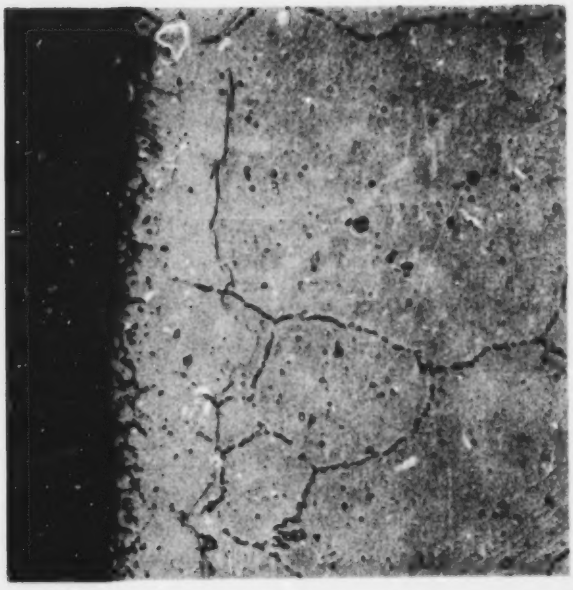
a. 1000X



b. 1000X



c. 1000X



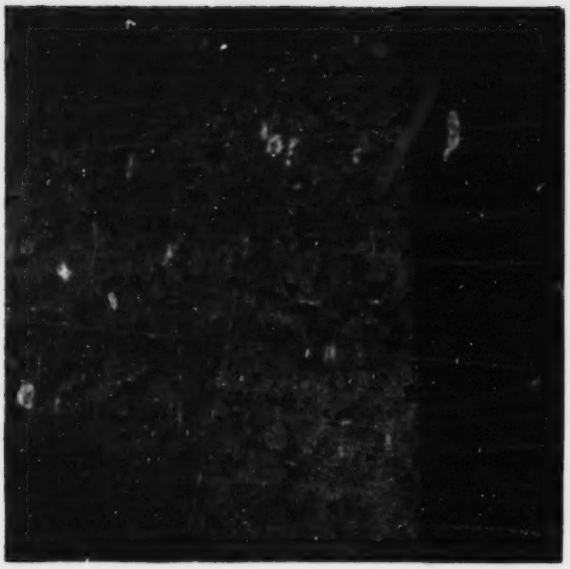
d. 500X

Fig. 3 -- Microstructures of Nimonic 80A:
(a) pre-test condition, (b) vacuum heat
treated, (c) heat treated in 1 atm air,
(d) after turbine (16) simulator corrosion test

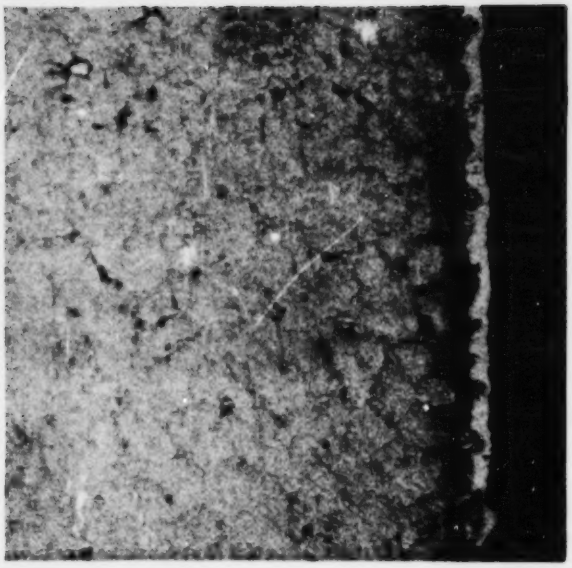
or corrosion test. Internal carbide precipitates can be clearly seen. The same material after heat treatment in vacuum is shown in Fig. 3b. A zone near the surface without precipitates is clear. The same heat treatment with the sample free standing in air (1 atm) is shown in Fig. 3c. A thin surface scale (about 0.06 mils thick), frequently spaced oxide channels, and oxide precipitates characterize the surface band outside the precipitate-depleted zone. These three photomicrographs are at a magnification of 1000X. Figure 3d is the corresponding structure after testing in the turbine simulator at a magnification of 500X. It is qualitatively similar to the structure in Fig. 3c, differing principally in the depth of the effected zones. The qualitative characteristics were not changed by length of exposure to the corrosive environment, only the depths of the zones increased with extended time.

A similar sequence of the Nimonic 105 microstructure is presented in Fig. 4. The designations are as before. In this case, the precipitate-depleted zone is much smaller and some fine structure is seen at the internal interface in the vacuum heat treated sample. This structure is not seen in the air-heat treated sample although the dimensions of the depleted zone are similar. In addition, pockets of oxidation at the surface, relatively widely spaced, are seen. Very little scale beyond the oxidation pockets is detectable. Qualitatively, the microstructure is the same as that of the corrosion tested alloy.

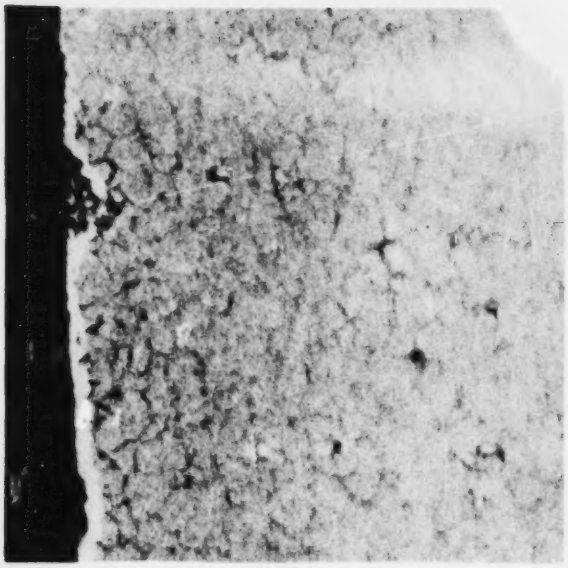
An unexplained feature in the corrosion tested Nimonic 105 is the depth of the precipitate-depleted zone. It is greater than that of the sample heat-treated in air, yet the extent of oxidation is not similarly greater. A point analysis traverse on the SEM failed to detect a concentration gradient which would justify an explanation involving preferential loss of an alloy component with accompanying increase in precipitate solubility. This explanation is not ruled out if the lost component is carbon which has too low an atomic number for detection on the SEM.



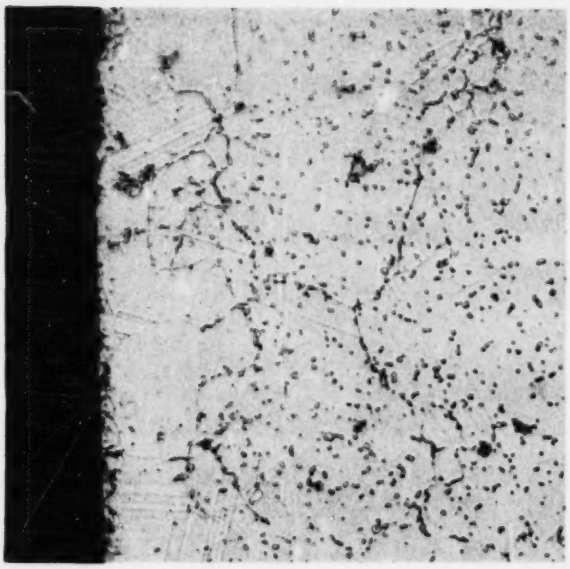
a. 1000X



b. 1000X



c. 1000X



d. 500X

Fig. 4 -- Microstructures of Nimonic 105
(a) pre-test condition, (b) vacuum heat treated, (c) heat treated in 1 atm air, (d) after turbine simulator corrosion test

The quantitative aspects of these phenomena are illustrated in Fig. 5, which shows the growth of the oxide penetration and precipitate-depletion zones in Nimonic 80A and Nimonic 105 as a function of time in the turbine simulator. The oxidation of Nimonic 105 is small compared to the overall metallurgical change. The zone growth-rates generally decrease with extended time; however, there is no indication of a limit, or saturation level, to the extent of the precipitate depletion effect within this scope of testing.

Dwg. 6169A35

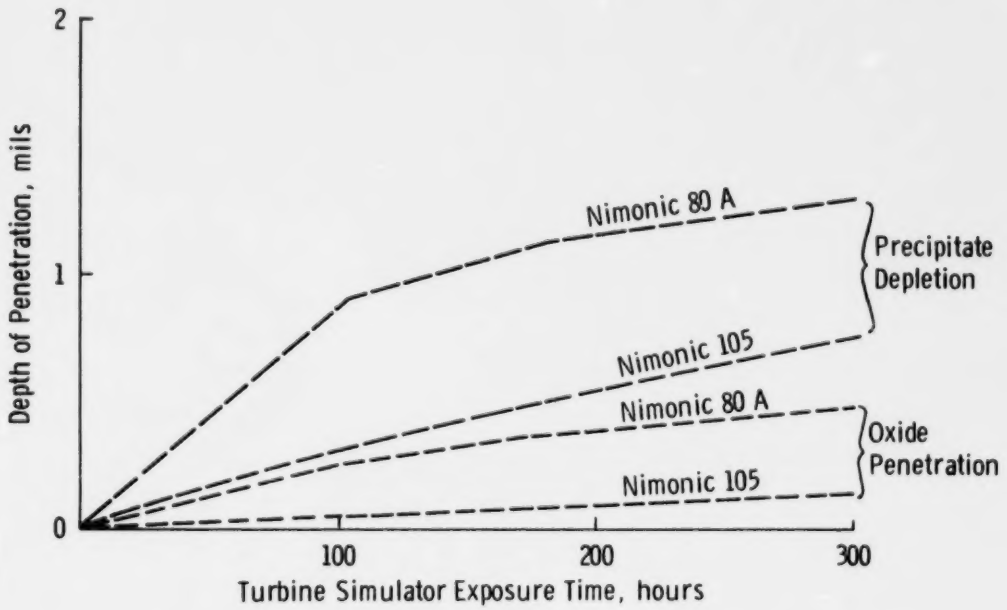


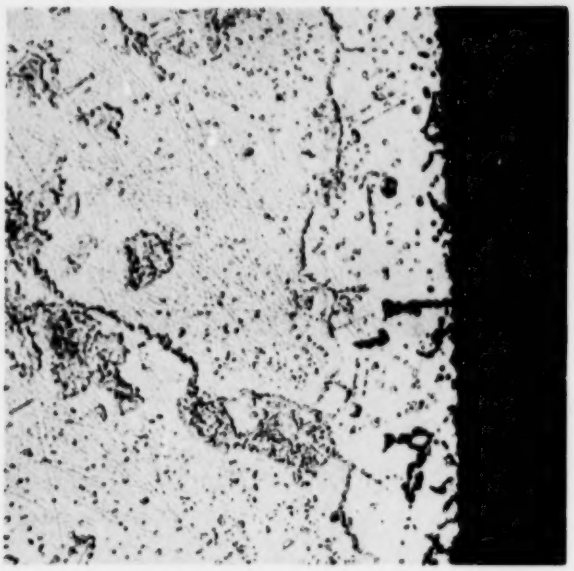
Fig. 5 -- Rates of metal degradation in turbine simulator corrosion tests

Four alloys were picked for testing at representative Westinghouse and G. E. Turbine inlets conditions. Two cobalt-base alloys, X-45 and FSX-414, are typical of the materials used for stationary components. Two nickel-base alloys, Udimet-500 and Udimet-710 are typical of the materials used for rotating parts.

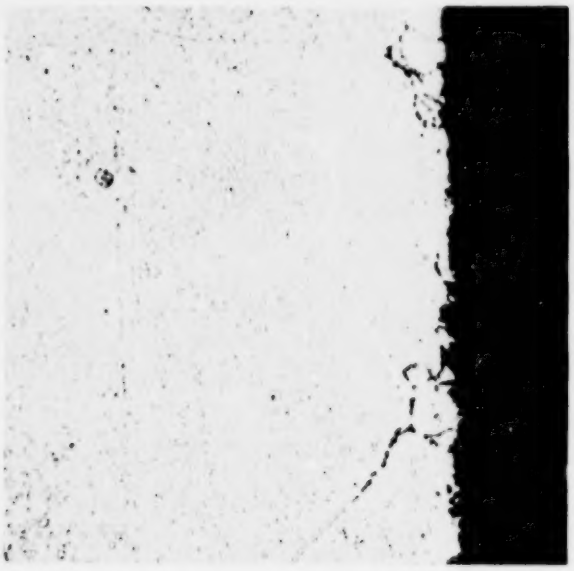
The two bands of effected alloy seen in the specimens were similar to those previously discussed. FSX-414 had the most variable depth of oxide penetration. The precipitate depletion in this alloy is related to the grain structure, so that the zone boundary is irregular, corresponding to the carbide-decorated grain boundaries one grain diameter in from the surface.

The oxide penetration in X-45 occurred at fewer sites, but tended to spread laterally as well as inward. The depths of both oxide penetration and precipitate depletion were more uniform, which may be due to a layer of small, recrystallized grains at the surface. Microstructures typical of these samples are shown in Fig. 6.

The two nickel-base alloys behaved similarly. Oxide penetrations and internal oxides formed a uniform zone of attack just inside the surface. The precipitate depletion also followed a regular pattern with a smooth zone boundary. Both effects penetrated more deeply in the specimen where grain boundaries intersected the surface. Representative microstructures are presented in Fig. 7. Quantitative penetration data for both cobalt and nickel base alloys are given in Table VI. The rates are based on one hundred hours of exposure, and extrapolations based upon them are expected to be higher than would be determined with data from longer test times. The data are presented as uniform recession values despite local variations since no significant leading edge/trailing edge effects were observed.



a. 500X



b. 500X

Fig. 6 -- Microstructures of cobalt base alloys after 100 hours in the turbine simulator at 1600°F, 105 psia
(a) FSX-414, (b) X-45

a. 500X

b. 500X

Fig. 7 -- Microstructures of nickel base alloys after 100 hours in the turbine simulator at 1600°F, 105 psia (a) U-500, (b) U-710

TABLE VI -- CORROSION AT 1600°F, 105 PSIA, 100 HOURS EXPOSURE

Alloy	Oxide Penetration, mils Range	Oxide Penetration, mils Weighted Ave.	Precipitate Depletion, mils Range	Precipitate Depletion, mils Weighted Ave.	Critical Degradation Rate, mils/hr*
FSX-414	0.2-0.6	0.3	0.4-0.7	0.55	0.003
X-45	0.15-0.25	0.2	0.3-0.6	0.5	0.002
U-500	0.2-0.4	0.25	0.4-0.6	0.5	0.005
U-710	0.1-0.25	0.2	0.2-0.5	0.4	0.004

* Based on weighted averages of oxide penetration for stator materials and precipitate depletion for rotor materials.

5.0 DISCUSSION AND CONCLUSIONS

Alloys for gas turbine applications are developed principally for high temperature strength and corrosion resistance. The alloys tested in this project derive their high temperature strength and creep resistance mainly from two mechanisms: solid solution strengthening and dispersion strengthening. The first of these is attributable to the variation in atomic size among the components of the continuous phase of the alloy. Dispersion strengthening occurs as a result of the interaction between precipitate particles and dislocations, the movement of the dislocations being impeded by precipitates.

All of the alloys considered contain carbide (or carbonitride) precipitates similar to those found in steels. These fall mainly into categories typified by TiC, $Cr_{23}C_6$, and Cr_7C_3. Some of the carbides precipitate in grain boundaries, some within the grains. The nickel-base alloys also contain a fairly uniform dispersed precipitation of $Ni_3(Al,Ti)$ called "gamma prime phase" (γ'). This γ' phase is responsible for the major dispersion strengthening effects in these alloys.[5]

Turbine design life is based upon the creep resistance of the alloys used. A loss of creep resistance could alter the expected useful lifetime of the machine. Therefore, the loss of dispersion strengthening in the precipitate depleted zone near the surface of the samples was considered with concern. A loss of dispersion strengthened creep resistance in a sufficient volume of metal in a highly stressed region of a turbine blade could lead to a distortion of the component. For this reason, precipitate depletion was considered to be the critical form of metal degradation of rotor materials observed in the tests.

The precipitate depletion rate, then, becomes the critical rate for estimating component lifetimes in the simulated environment. The engineering estimate for tolerable metal wastage on W-251 blades and vanes in current usage is 40 mils. The same limit was used for the G.E. materials, and a limit of 20 mils was adopted for the Ruston turbine conditions by scaling down to the smaller sized components for that machine. On these bases, the minimum projected lives are about 8,000 to 10,000 hours for the Westinghouse and G.E. turbines, and about 8,000 hours for the series TA 1500 turbines. These estimates were made by linear extrapolation of the metal degradation data of Fig. 5 and Table VI for blade alloys. Limitations due to corrosion applied to the alloys used for non-moving parts resulted in longer lifetime estimates. These conclusions are dependent on no changes occurring in the corrosion behavior of these systems after times long in comparison to the 100 and 300 hour tests on which they are based. The machines simulated would be expected to have blade lifetimes in excess of 20,000 hours with high quality fuel, depending on the mode of usage. In all cases, durability is sensitive to operating parameters. Increasing number of startups decreases durability; base loaded machines are more durable (in terms of hours of operation) than load following machines.

Aside from the development of precipitate depleted zones, no environmental effects on the samples were observed other than oxidation. Despite the additions of sulfur, chlorine, sodium, potassium, and magnesium to the fuel, no sulfidation or hot-corrosion attack occurred. Moreover, there was no increase of the oxidation rate. The rates observed in turbine simulator tests were compatible with rates observed in standing, one atmosphere air, which were, in turn, compatible with data reported in the literature[7]. Yet, the effects of those additives in increasing corrosion are well known and documented[6,8,9].

Miller and Krause[10] have shown that corrosive species in incinerator deposit build up with time, concentrating by diffusion inwards towards the collecting surface. Thus, the thermodynamic

activities of corrosive agents can build up near the corroding surface although the activities of the same species are relatively low in the flue gas. In attempting to simulate refuse combustion in a fluidized bed, a deposit was produced which built up to some thickness, then spalled, to expose the scaled metal surface whereupon deposition began again. This cyclic deposition may explain the apparent contradiction in the preceding paragraph.

If the time required to concentrate the corrosive agents sufficiently to effect the corrosion rate is greater than the time required for the deposit to build up to the spalling level, then whatever concentration has been achieved is lost when a chip of deposit falls off, and the concentration process must start over from the beginning. It is speculated, then, that the observed lack of corrosion enhancement was dependent on the nature of the deposit. Therefore, the validity of applying the results of this study to the products of refuse combustion in a fluidized bed may depend on the nature of the solids produced.

Clearly, the test conditions represent the best simulation of the CPU-400 pilot plant and prototype available at this time; however, the simulation is not completely identical. The difference in combustion temperature is likely to be the source of differences in the silicate structures produced in the two types of combustor. It is recommended that, in the period before long time semi-continuous operation of the fluidized bed system is feasible, valuable information may be gained by the collection and structural analysis of the solids in the fluidized bed combustion products. Experience in this project has suggested that sampling combustion product solids by attempting to withdraw them from the system, while still entrained in the flue gas, through a probe, is inadequate. This conclusion is supported by the differences between the analyses of the probe-sampled flyash and the deposit scraped from corrosion test samples. Therefore, collectors

should be inserted in the flue gas stream for the duration of fluidized bed combustion runs; ten to twenty hours of exposure should be more than adequate to provide sufficient material for spectroscopic and diffraction analyses. Once the deposit from fluidized bed combustion is well characterized, further corrosion tests can be planned.

6.0 ACKNOWLEDGMENTS

This report was the responsibility of the author. The conclusions of the project, however, are the result of the work of several others as well. In particular:

Dr. W. E. Young and Dr. S. Y. Lee developed the turbine simulator equipment, and their knowledge and experience kept the tests operating correctly.

Dr. C. J. Spengler contributed greatly to the interpretation of alloy microstructural data and relating them to known corrosion behavior.

Mr. L. Paulukonis moved the 300 pound simulator sections and measured the one hundredth of a milligram sample weight changes; a weighty job well done.

The author especially wishes to thank Mr. Michael Daugherty of the International Nickel Company for his help in obtaining sample quantities of the alloys tested.

7.0 REFERENCES

1. Outlook Editor, Environmental Science & Technology, 4, 631-633 (1970).
2. Personal Communication, M. Eyster, Manager of Sales, Turbo-Machinery, Mid-Continent Supply Co. (August 1971).
3. Personal Communication, P. M. Jarvis, Product Planner, G.E. Gas Turbine Operational Planning, to B. T. Riley, Jr., EPA (September 1971).
4. Technical Report TR 71-10 and Addendum No. 1, "Test Report for the Qualitative and Quantitative Analysis of Off-Gases and Fumes From a Fluid Bed Combustor Burning Municipal Refuse," Combustion Power Company, Inc. (August 1971).
5. P. D. Pepe and G. M. Turner, "Designe of the First Large United Kingdom Power Producing Refuse Disposal Plant," Journal of Engineering for Power, 239-251 (July 1970).
6. S. Y. Lee and W. E. Young, "Corrosion Testing of High-Temperature Gas Turbine Alloys," Presented in Cranfield Propulsion Symposium, Cranfield, England (1969).
7. W. Betteridge, The Nimonic Alloys, Edward Arnold (Publishers) Ltd., London (1959).
8. P. S. Gray, Discussion of "Corrosion of High Temperature Nickel-Base Alloys by Sulfate-Chloride Mixtures" by Lewis and Smith, First International Congress of Metallic Corrosion, Butterworths, London, p. 213 (1961).
9. P. A. Alexander, "Laboratory Studies of the Effect of Sulphates and Chlorides on the Oxidation of Superheater Alloys," ibid., p. 571 (1961).
10. P. D. Miller, H. H. Krause, et al., "Fireside Metal Wastage in Municipal Incinerators," 2nd Annual Summary Progress Report to SWMO, EPA (Research Grant No. EC 00325-02) (April 1971).

APPENDIX A

Additives to Diesel Fuel to Simulate Refuse Combustion

Element	Chemical Form	Concentration, wt.%	Manufacturer	lbs. added/ gal. fuel	Calculated ppm oxide in flue gas
Si	proprietary organometallic	15.42	Perolin	10.46×10^{-4}	0.8
Al	aluminum sulfonate	15.6	Conoco	7.38×10^{-4}	0.5
Na	sodium naphthenate	4.0	Mooney Chem. Co.	8.07×10^{-4}	0.1
K	potassium carboxylate	8.0	"	2.71×10^{-4}	0.06
Ca	calcium naphthenate	8.0	"	7.77×10^{-4}	0.2
Mg	magnesium acid neodecanoate	3.0	"	5.25×10^{-4}	0.06
Fe	iron carboxylate	12.0	"	2.54×10^{-4}	0.1
Cl	trichlorethylene	81.05	---	4.69×10^{-2}	90
S	present in fuel	0.07	---		
	plus added with aluminum	1.89	---	7.38×10^{-4} (total)	37.8